

PATENT SPECIFICATION

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 6K8X



(54) SELF-BONDING TWO-PACKAGE ROOM TEMPERATURE VULCANIZABLE SILICONE RUBBER COMPOSITIONS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to room temperature vulcanizable silicone rubber compositions and in particular the present invention relates to self-bonding two-package room temperature vulcanizable silicone rubber compositions.

Room temperature vulcanizable silicone rubber compositions are well known. Such silicone rubber compositions are divided in two types, the one-package room temperature vulcanizable silicone rubber composition and the two-package room temperature vulcanizable silicone rubber compositions.

The present invention provides a room temperature vulcanizable silicone rubber composition comprising,

- (a) a linear, organopolysiloxane containing terminal silicon-bonded hydroxy groups and having a viscosity of 500 to 10,000,000 centipoises when measured at 25° C, the organic groups of the aforesaid organopolysiloxane being substituted or unsubstituted monovalent hydrocarbon radicals,
 (b) from 5 to 300% by weight, based on organopolysiloxane, of a filler,
 (c) from 0.1 to 15% by weight, based on organopolysiloxane, of
 (1) an organoxysilane or silicate corresponding to the general formula,



(1)

where R is a monovalent hydrocarbon or halogenated hydrocarbon radical and R¹ is an alkyl, haloalkyl, aryl, haloaryl, alkenyl, cycloalkyl, cycloalkenyl, cyanoalkyl, alkoxy or acyloxy radical, or

- (2) a liquid partial hydrolysis product of the aforementioned organoxy silane or silicate compounds,
 (d) from 0.1 to 5% by weight, based on the organopolysiloxane, of a catalyst which is metal salt of an organic monocarboxylic or dicarboxylic acid in which the metal ion is lead, tin, zirconium, antimony, iron, cadmium, barium, calcium, titanium, bismuth or manganese, and
 (e) from 0.1 to 10% by weight, based on the organopolysiloxane, of a nitrogen-containing silane of the formula:



(2)

where R is a monovalent hydrocarbon or halogenated hydrocarbon radical, Q is

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an alkoxy, phenoxy, halo, amino or dialkylamino group, and Q' is a saturated, unsaturated or aromatic hydrocarbon residue substituted by at least one amino hydrazone, azirane or, cyano group, and optionally one or more thio, sulphone, oxa, oxo, diorganosilicon and/or ester groups, and a is 0, 1 or 2.

These compositions are self-bonding, i.e. they do not require the use of a primer. The presence of the nitrogen-containing silane in an amount of 0.1 to 10%, by weight, based on the linear organopolysiloxane (a) imparts the desired self-bonding properties to the room temperature vulcanizable silicone composition. The nitrogen-containing silane (c) acts both as a self-bonding agent and as a catalytic agent in the composition. The composition, however, also contains an additional catalyst constituted by from 0.1 to 5% by weight, based on organopolysiloxane, (a) of a catalyst which is a metallic salt of an organic monocarboxylic or dicarboxylic acid in which the metal ion is lead, tin, zirconium, antimony, iron, cadmium, barium, calcium, titanium, bismuth or manganese. Preferred nitrogen containing silanes (c) have the formula,

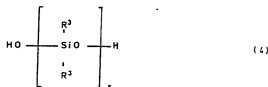


where R^2 is a monovalent hydrocarbon or halogenated hydrocarbon radical of up to 10 carbon atoms, most preferably an alkyl radical of 1 to 5 carbon atoms; a has the meaning given above and preferably has a value of 0.

The filler that is used in the present composition may be a reinforcing filler or semi-reinforcing filler selected from titanium dioxide, lithopone, zinc oxide, zirconium silicate, silica aerogel, iron oxide, diatomaceous earth, calcium carbonate, fused silica, precipitated silica, glass fibers, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, asbestos, carbon black, graphite, cork, cotton and synthetic fibers. The preferred filler for the present application is, of course, fumed silica and precipitated silica and particularly fused silica or precipitated silica that has been treated with various types of siloxane compositions.

The present composition may additionally include a branched or straight polymer compound composed of $(R^3)_2SiO$ units, $(R^3)SiO_{1/2}$ units and $R^3SiO_{1/2}$ units having 0.05 to 8% by weight, preferably 0.1 to 8% by weight of hydroxy radicals (the viscosity of the polymer being preferably between 500 to 1.0×10^5 centipoise at 25° C). The ratio of the organosiloxy units to the diorganosiloxy units is from 0.11 to 1.4 and the ratio of the triorganosiloxy units to the diorganosiloxy units is from 0.02 to 1, inclusive.

The preferred linear fluid organopolysiloxane containing terminal silicon-bonded hydroxy groups and having a viscosity of 500 to 10,000,000 centipoises when measured at 25° C, has preferably the formula,



where R^1 is a monovalent hydrocarbon or halogenated hydrocarbon radical and r is a whole number from 250 to 7,275. The radicals R , R^1 , and R^2 are preferably alkyl radicals, such as methyl, ethyl, propyl, butyl or hexyl; aryl radicals, such as phenyl, or diphenyl; alkaryl radicals such as tolyl, xylol, or ethylphenyl; aralkyl radicals such as benzyl, or phenylethyl; haloaryl and haloalkyl such as chlorophenyl, tetrachlorophenyl, or difluorophenyl; and alkenyl radicals such as vinyl or allyl. Further, R^2 may also represent cyanoalkyl, cycloalkyl or cycloalkenyl radicals. The R^1 groups attached to a single silicon radical may be the same groups or different groups. It has been found that at least 50% and preferably 70 to 100% of the R^2 groups in the diorganopolysiloxane molecule should be methyl. Further, the diorganopolysiloxane can be a homopolymer, or a copolymer having different types of units in the chain such as dimethyl, diphenyl, or methyl-phenyl.

The organopolysiloxanes of formula (4) may also be represented by the average unit formula,

(5)



where R³ is defined above and the value of *m* may vary from 1.99 to 2. The above average unit formula only represents organopolysiloxanes having monofunctional terminal groups and optional trifunctional units. However, in the present case, it is preferred that the terminal groups be hydroxy and the monofunctional and trifunctional groups be kept to a minimum.

Preparation of the diorganopolysiloxanes of formulae (4) and (5) may be carried out by any of the procedures well known to those skilled in the art. Such polysiloxanes can be produced by hydrolysis of one or more hydrocarbon substituted dichlorosilanes in which the substituents consist of saturated or unsaturated hydrocarbon groups to produce a crude hydrolyzate containing a mixture of linear and cyclic polysiloxanes. The crude hydrolyzate is then treated with a suitable catalyst such as KOH so that it can be depolymerized to form a mixture of low boiling, low molecular weight cyclic polymers and undesirable materials such as the monofunctional trifunctional chlorosilane starting material. The resulting composition is fractionally distilled and there is obtained a pure product containing the low boiling, low molecular weight cyclic polymers free of any significant amount of monofunctional and trifunctional groups.

In order to depolymerize the crude hydrolyzate, there is added to said hydrolyzate, KOH and a diphenyl solvent and the mixture is heated at a temperature in the range of 150° C to 175° C under an absolute pressure of 100 mm of Hg. to produce and remove by evaporation a product consisting of low molecular weight cyclic polysiloxanes comprising, for example, about 85 percent of the tetramer and 15 percent of the mixed trimer and pentamer. Among the cyclic polymers that may so be produced are hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane. There also may be formed mixtures of cyclopentasiloxanes such as a mixture of octamethylcyclotetrasiloxane and tetraethyltetramethylcyclotetrasiloxane, and mixtures of cyclic polymers of dimethylsiloxane with cyclic polymers of diphenylsiloxane, cyclic-methylphenylsiloxanes and cyclicmethylvinylsiloxanes.

The pure cyclic polysiloxanes are mixed in the desired proportions to obtain the above defined mixture. Then the mixture of the cyclic polysiloxanes is subjected to an equilibration procedure to obtain the diorganopolysiloxane of formula (4). The equilibration is preferably carried out at temperatures of 125° C to 150° C in the presence of a small amount of rearrangement catalyst such as potassium hydroxide, or tetrabutyl phosphonium hydroxide. The amount of catalyst used will depend on the extent of the polymerization desired. Generally, 5—10 ppm (parts per million) of the catalyst is sufficient for the polymerization to produce diorganopolysiloxane polymers of a viscosity of 5.0×10^2 to 1.0×10^3 centipoises measured at 25° C. There is also present in the reaction mixture 15—150 ppm (parts per million) of water, based on the cyclic polymer, so as to supply the hydroxy groups which function as chain-stoppers for the linear diorganopolysiloxane material that is formed. After the equilibration reaction has proceeded for two hours, there is reached an equilibration point wherein the mixture contains about 85% linear polymers and the amount of linear polymers being formed from the cyclic polymers is equal to the cyclic polymers being formed from the linear polymers.

When this equilibration point has been reached, there is added to the mixture a sufficient amount of an acid donor to neutralize the KOH catalyst so as to terminate the polymerization reaction. Preferably, 1.7 parts per million of tris - (2 - chloroethylphosphite) are added to the reaction mixture to liberate HCl, which reacts with and neutralizes the KOH and so terminates the equilibration reaction. The cyclicdiorganopolysiloxanes in the reaction mixture are then distilled off to leave the polydiorganopolysiloxane gum which is useful in the present invention. The resulting linear diorganopolysiloxanes are chain-stopped primarily with hydroxy groups and have a viscosity of 5×10^2 to 1.0×10^3 centipoise at 25° C. Further, the number of diorgano substituent groups in the siloxane chain is at least 2,150.

High molecular weight diorganopolysiloxanes having a viscosity of 5×10^3 centipoise at 25° C and above can be treated with water to arrive at low molecular

weight diorganopolysiloxanes having a viscosity of 500 to 5×10^3 centipoise at 25° C. This may be accomplished by blowing steam across the surface of the high molecular weight product, or through the polymer, for a sufficient length of time to obtain the low molecular weight component having the desired silanol content. Thus, it is desirable to obtain the low molecular weight diorganopolysiloxane of formula (3) from a portion of the high molecular weight diorganopolysiloxanes by the above water treatment, well known to those skilled in the art, so as to reduce the number of diorganosiloxy units from above 7,275 to a value of 250 to 2,150. The use of steam in this fashion will cause a decrease in the viscosity of the polymer, while at the same time the formed linear polysiloxane will have terminal silicon-bonded hydroxy groups.

Alternatively, the low molecular weight diorganopolysiloxanes can be produced from the high molecular weight diorganopolysiloxane by adding water to them and heating the resulting composition at elevated temperatures of 150° C to 170° C so as to break up the long chain polymers into smaller chains. The amount of water used will vary depending upon such factors as the molecular weight of the polymer being treated, the time and the temperature at which the mixture of high molecular weight diorganopolysiloxanes are heated and the desired viscosity. These conditions may readily be determined, for example, a high molecular weight diorganopolysiloxane having a viscosity of 2,000,000 centipoise at 25° C may be heated to 150° C with 0.5 percent by weight of water for two hours to arrive at a low molecular weight organopolysiloxane of formula (3) having a viscosity of 2,000 centipoise. Preferably, the low molecular weight organopolysiloxane is produced so that it has a viscosity of 2,000 to 3,000 centipoise at 25° C.

In order for the diorganopolysiloxane fluids to cure there must be present in the composition the cross-linking agent of formula (1). In that formula, R groups may be alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, amyl, isoamyl, octyl, isooctyl, decyl, or dodecyl; haloalkyl such as the chlorinated, brominated, or fluorinated alkyl radicals. In addition, R may represent aryl, aralkyl and alkenyl radicals such as vinyl, allyl, phenyl, tolyl, xylyl, benzyl, phenylethyl, naphthyl, anthracyl, or biphenyl, as well as the halogen-substituted derivatives of the above radicals. In addition, R may represent cycloalkenyl, cycloalkyl and cyanoalkyl radicals. The radical R¹ represents the same radicals as R and, in addition, preferably represents alkoxy or aryloxy radicals such as methoxy, ethoxy, butoxy and phenoxy.

Alternatively to the monomeric compounds of formula (1), liquid partially hydrolyzed products thereof can also be used as cross-linking agents. Such hydrolysis products are obtained by effecting partial hydrolysis in water of the particular monomeric compound in the presence of small amounts of acid to a point where it is still water-insoluble and still possible to isolate a liquid partially hydrolyzed organosilicon compound. Thus, the ethyl silicate having the formula $(C_2H_5O)_2Si$ may be partially hydrolyzed by adding acids or acid-forming metal salts, such as $FeCl_3$, $CuCl_2$, $AlCl_3$, or $SnCl_4$, to the liquid monomeric organosilicate, and thereafter effecting suitable hydrolysis of this mixture of ingredients in water to obtain the two-phase composition, from which the water-insoluble, partially hydrolyzed organosilicate can readily be separated from the aqueous phase and catalyst. A partially hydrolyzed ethyl silicate is sold under the tradename Ethyl Silicate-40, by Union Carbide Corporation.

There is added from 0.1 to 15.0%, by weight of the cross-linking agent of formula (1) (or its hydrolysis product) and preferably 0.1 to 10%, by weight, based on the weight of the diorganopolysiloxane of formulae (4) and (5). If more than 15.0%, by weight of cross-linking agent were to be used, the excess would not function as a cross-linking agent since the initial hydroxy positions on the organopolysiloxane would already have reacted with the cross-linking agent and the excess would act as a filler, reducing the elasticity of the cured silicone rubber composition. If less than 0.1%, by weight of cross-linking agent were to be used, there would not be sufficient cross-linking agent to react with the organopolysiloxane to form the cured silicone rubber.

Although the above mentioned cross-linking agents must be used, there may additionally be used as cross-linking agents, organopolysiloxane resins having a functionality greater than 2 and preferably greater than 2.5. The organopolysiloxane resins are methylsiloxanes, or resins which contain both monomethyl and dimethyl or monophenyl units. There may also be used ethylsiloxane resins, in which the ratio R¹:Si is 1.4 to 1 and which contains 15 mol % of butoxy groups, or there may be used resins in which the ratio R¹:Si is 1.1 to 1 and which contain 10 mol % of methoxy groups or there may be used methylphenylsiloxane resins containing 50 mol % of monomethyl units, 25 mol % of dimethyl units and 25 mol % of monophenyl units.

Other suitable additional cross-linking agents are organohydrogenpolysiloxanes of the formula,

(6)



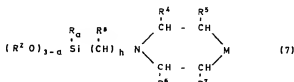
in which R^{37} is an alkyl or aryl radical and a is a number less than 2, but is not zero. The organohydrogenpolysiloxane cross-linking agents have the disadvantage that during curing there is evolved hydrogen gas which can result in bubbles being trapped in the silicone rubber composition. Although the above cross-linking agents can be used in the compositions, the organosilicates of formula (1) for their partial hydrolysis products) must be present since the processability of the composition is facilitated and the cured silicone rubber composition has better physical properties. A more detailed description of these other cross-linking agents is to be found in U.S. patent 3,127,363.

There is incorporated into the organopolysiloxane of formulae (4) and (5), a filler which may be of the reinforcing filler type or of the semi-reinforcing type. Generally, the reinforcing fillers have 100—300 square meter surface areas per gram while the semi-reinforcing fillers have a surface area of 1—20 square meters per gram.

The reinforcing fillers are added when it is desired to have a high strength silicone rubber composition, that is, a composition with high values for tensile strength and percent elongation. Illustrative of the many fillers which can be employed are titanium dioxide, lithopone, zinc oxide, zirconium silicate, silica aerogel, iron oxide, diatomaceous earth, calcium carbonate, fumed silica, precipitated silica, glass fibers, magnesium oxide, chromium oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, asbestos, carbon black, graphite, cork, cotton and synthetic fibers. There can also be used silica filler treated with an organosiloxane cyclic trimer or tetramer such that the filler is hydrophobic. Generally, there is added to said diorganopolysiloxane of formulae (4) and/or (5), 5 to 300% by weight of filler and preferably 10—200% by weight.

The other essential component in this silicone rubber composition is a catalyst. It has been found that only certain metallic salts of organic carboxylic acids and dicarboxylic acids, in addition to the nitrogen-containing silanes of formula (2), may be employed with the organopolysiloxanes of formulae (4) and (5) as a curing catalyst. Suitable acid radicals are the resinates, linoleate, stearate, and oleate, as well as the lower radicals such as acetate, butyrate, and octoate. Metallic salts of lauric acid have been found to be especially effective. The metal ion of the metal salt is lead, tin, zirconium, antimony, iron, cadmium, barium, calcium, titanium, bismuth or manganese. Thus, examples of suitable metallic salt catalysts are tin naphthenate, lead octoate, tin octoate, iron stearate, tin oleate, antimony octoate, tin butyrate, basic dibutyl tin laurate and dibutyl tin dilaurate. The tin and lead salts are preferred since they are usually soluble in the diorganopolysiloxanes of formulae (4) and (5) and since they have enhanced catalytic activity in combination with the alkyl silicate. It is important to note that other compounds which would be expected to exercise good catalytic activity in the mixture of diorganopolysiloxane, filler and alkyl silicate exercise no catalytic activity whatsoever. This class of compounds are zinc salts of organic acids, cobalt oleate, cobalt naphthenate, manganese naphthenate, nickel naphthenate and calcium stearate. From 0.1 to 5% by weight of the metallic salt is used, based on the weight of the diorganopolysiloxane.

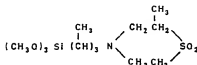
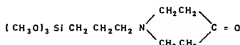
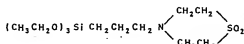
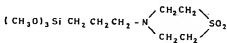
One specific nitrogen containing silane coming within the scope of formula (3) above is a compound having the formula,



wherein R and R^2 are each a monovalent hydrocarbon or halogenated hydrocarbon radical and preferably may be selected from the various types of radicals disclosed above for the R^2 radical in formula (5). Preferably, R and R^2 are alkyl or aryl radicals of 1 to 10 carbon atoms, and preferably have 1 to 5 carbon atoms. The radicals R^4 , R^5 , R^6 , R^7 and R^a in formula (7) above are each hydrogen, or an alkyl or aryl radical

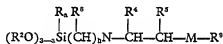
of up to 10 carbon atoms, M is SO₂ or C=O, *h* is a whole number from 3 to 20 and, as pointed out previously, *a* is 0, 1 or 2.

Compounds falling within the scope of formula (7) above which are preferred in the present invention for particularly providing desirable bonding properties for the resulting composition are as follows:



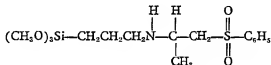
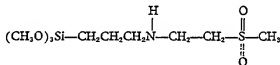
Another class of compounds coming within the scope of formula (3) above has the formula,

(8)



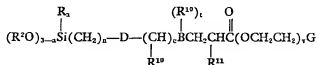
where R¹, R², R³, R⁴, R⁵, M, *a* and *h* are as previously defined, and R⁶ is a monovalent hydrocarbon or halogenated hydrocarbon radical.

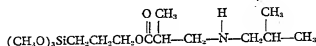
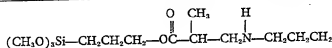
Compounds coming within the scope of formula (8) and which are preferred in the present application are as follows:



Another group of nitrogen-containing silanes coming within the scope of formula (3) above has the general formula,

(9)

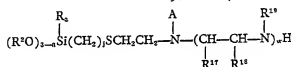




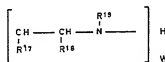
For more information as to the compounds of formula (10) above one is referred to U.S. Patent No. 3,700,716.

Another class of nitrogen containing silanes which are within the scope of formula (3), has the formula,

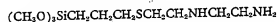
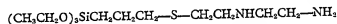
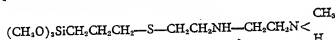
(11)



where R, R² and a are as previously defined, R¹⁷, R¹⁸ and R¹⁹ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, j is a whole number from 2 to 20, w is a whole number from 1 to 500, and A is hydrogen, or an alkyl radical, an aryl radical or



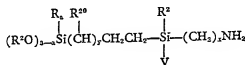
Compounds which are preferred in the present application and which come within the scope of formula (11) above, are as follows:



The compounds of formula (11) are more fully disclosed and discussed in U.S. Patent No. 3,700,715.

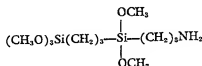
Another nitrogen containing silane coming within the scope of formula (3) above is

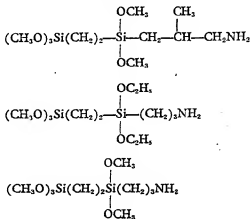
(12)



where R, R² and a are as previously defined, R²⁰ is hydrogen or an alkyl or aryl radical, V is R or R²O—, y is 0 or a whole number from 1 to 20, and x is a whole number from 2 to 20.

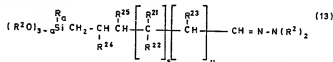
Preferable compounds which come within the scope of formula (12) above, are as follows:





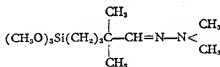
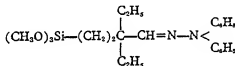
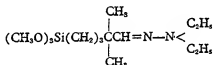
The compounds disclosed in formula (12) above are more fully described and disclosed in U.S. Patent No. 3,729,496 and 3,773,819.

Another class of nitrogen containing silanes coming within the scope of formula (3) above, has the formula,



where R, R² and a are as previously defined, R²¹, R²², R²³, R²⁴ and R²⁵ are each hydrogen, or an alkyl, cyclosilyl or aryl radical of up to 10 carbon atoms, r is 0 or 1, and u is 0 or a whole number from 1 to 20.

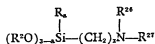
The preferred compounds coming within the scope of formula (13) above are as follows:



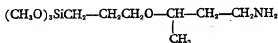
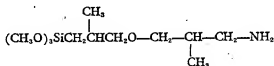
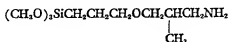
For further information as to the compounds of formula (13) above, and to the synthesis thereof the reader is referred to U.S. Patent No. 3,700,711.

Another class of nitrogen containing silanes coming within the scope of formula (3) has the formula,

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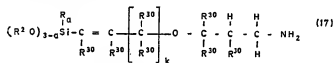


where R, R² and a are as previously defined, R²⁶ and R²⁷ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, and x is a whole number from 2 to 20.



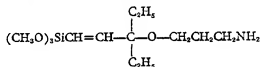
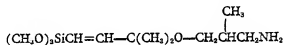
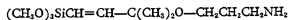
The synthesis of the compounds of formula (16) above is to be found in U.S. patent No. 3,598,853.

An additional class of nitrogen containing silanes coming within the scope of formula (3) has the formula,



where R, R² and a are as defined previously, each symbol R³⁰ is hydrogen, a C₁-C₆ alkyl radical, a cycloalkyl radical containing up to 7 carbon atoms, a mononuclear or binuclear aryl radical, a mononuclear aryl C₁-C₆ alkyl radical or two radicals R³⁰ attached to the same carbon atom can, taken together with that carbon atom form a cycloalkyl radical, and k is a whole number from 1 to 9.

Preferred compounds coming within the scope of formula (17) above are as follows:

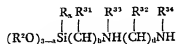


The nitrogen containing silanes coming within the scope of formula (17) above are more fully disclosed and discussed in U.S. patent No. 3,549,590.

The above compounds of general formulae (7) to (17) are preferred nitrogen-containing silanes of formula (3). They provide self-bonding properties when incorporated into the two-package room temperature vulcanizable silicone rubber compositions according to the present invention, as well as acting as catalytic agents.

Alternatively to the above nitrogen containing silanes, other nitrogen containing silanes coming within the scope of formula (3) have the formula,

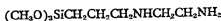
(18)



where R, R² and a are as defined previously, R²¹, R²², R²³ and R²⁴ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, and b and d are whole numbers from 2 to 10.

Compounds coming within the scope of formula (18) above which are preferred

in the self-bonding two-package room temperature vulcanizable silicone rubber composition of the present invention are as follows:

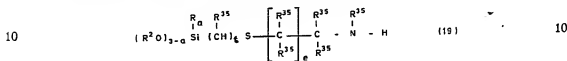


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The compounds of formula (18) above are more fully described in U.S. patent No. 2,971,864.

Another sub-generic class of nitrogen containing silanes coming within the scope of formula (3) above are those silanes having the formula,



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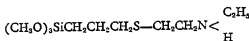
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where R, R² and a are as previously defined, each symbol R³⁵ is hydrogen or an alkyl or aryl radical of up to 10⁶ carbon atoms, e is a whole number from 1 to 10, and f is a whole number from 2 to 10.

Preferred compounds coming within the scope of formula (19) above are as follows:

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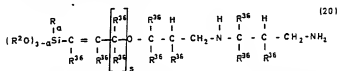


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The compounds of formula (19) above are more fully described in U.S. patent No. 3,488,373.

Another preferred class of nitrogen containing silanes which come within the scope of formula (3) above comprises silanes of the formula,



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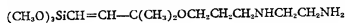
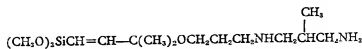
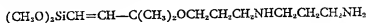
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where R, R² and a are as previously defined, each symbol R³⁶ is hydrogen, or an alkyl radical, aryl radical, cycloalkyl radical containing 5 to 7 carbon atoms, mononuclear or binuclear aryl radical, mononuclear aryl C₁-C₈ alkyl radical or two radicals R³⁶ attached to the same carbon atom can, taken together with that carbon atom form a cycloalkyl radical, and f is a whole number from 1 to 4.

Preferred compounds coming within the scope of sub-generic formula (20) above are compounds of the formula,

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The compounds of formula (20) above are more fully disclosed in U.S. patent No. 3,549,590.

In applying the components that are present in the room temperature vulcanizable composition of the present case, the linear diorganopolysiloxane is mixed with filler and color pigments and then stored separately. A second mixture is then composed of the alkyl silicate the metal salt catalyst, and the nitrogen-containing silane, with or without a solvent such as xylene. As a result of the above, there are two mixtures formed, one the base polymer which is stored separately and the other the curing catalyst system which is stored separately. When it is desired to produce the cured room temperature vulcanizable composition, the base polymer is mixed with the curing catalyst mixture and the material is spread, rolled, molded or applied in one manner or another to the desired application. It should be noted that once these two components are mixed together, there is approximately 10 minutes work time available to mix the two components together and to mold the resulting mixture into the desired surface. Within 20 to 30 minutes after the initial mixture of the components is carried out at ambient temperature, the materials have achieved a sufficient degree of cure (Shore A Hardness 15) to have assumed a definite form. After 1 hour, the silicone rubber composition cures to approximately 80% of the final Shore A Hardness. After 6 hours very little additional change of Hardness occurs. Preferably, the mixture of the base polymer and the curing agent composition is allowed to cure for 24 hours in whatever application it is put to, so that it develops its full properties as a room temperature vulcanizable silicone composition. The two-package room temperature vulcanizable silicone rubber composition may be used to form various types of silicone rubber materials. Such a composition may also be used to form coatings for various applications such as for coating cloth or for coating roofs.

When the room temperature vulcanizable silicone rubber composition is to be used for coating roofs, then it is desirable to disperse the base polymer, i.e., the mixture of the linear diorganopolysiloxane, filler and coloring agent in one of the common hydrocarbon solvents available for that purpose, for example, inert hydrocarbon solvents such as benzene, toluene, mineral spirits, and cyclohexane. When such a solution is formed of the base polymer in the solvent, it is desirable to form a solution in which the solvent forms 5 to 50% by weight of the solution and the base polymer which comprises the linear diorganopolysiloxane, the filler and the coloring pigment forms from 50 to 95% of the solution. This solution of the base polymer is then mixed with a curing agent catalyst composition as disclosed above and the solution or mixture of the two is then applied or coated on roofs or draperies and other type of objects. It should be noted that the room temperature vulcanizable silicone rubber composition is especially suited for coating roofs and that it adheres very strongly and forms a cohesive bond between the roofing substrate and the silicone rubber composition. In addition, roofing granules can be applied to the top of the present two-package room temperature vulcanizable coating composition and such granules will adhere very strongly to the cured silicone rubber composition of the present case.

The nitrogen containing silane is preferably used at a concentration of 0.1 to 5%, by weight, more preferably in a concentration of 0.5 to 4% by weight, based on the linear diorganopolysiloxane.

There may also be present in the composition certain oxygen-containing solvents which will prolong the work life of the composition without retarding the final cure. The use of such solvents may prolong the work life or the pot life of the composition by at least a factor of 2, but after the silicone rubber composition has been spread out to dry, the solvents evaporate quickly allowing the silicone rubber composition to cure rapidly. Oxygen-containing solvents that may be used are the alcohols, ether solvents, ester solvents, ketone solvents and alcohol ether solvents such as acetone, methanol, isopropanol, butyl ether, ethyl acetate, isomylketone and ethylene glycol methyl ether.

The following examples in which all parts are percentages are by weight unless otherwise indicated, are given for the purpose of illustrating the invention and are not intended to limit the invention in any way or manner.

EXAMPLE 1.

There is prepared a base polymer solution comprising 100 parts of dimethylpolysiloxane oil which is hydroxy stopped and has a viscosity of 5000 centipoise at 25° C, 160 parts of ground silica filler, 2.0 parts of hydrogenated castor oil, 6.4 parts of titanium dioxide and 1.6 parts of ceramic black. The above components are mixed together. Then 80% of the above composition is mixed with 20% of mineral spirits solvent. The above composition forms the base polymer solution.

The base polymer solution is mixed with the catalytic composition containing the catalyst, the nitrogen containing silane and the ethyl silicate dissolved in a solvent. The composition of the catalyst mixture is shown in Table I below. Further, in Table I below there is shown the weight of the catalyst composition used per 100 parts by weight of the polymer solution defined above. The resulting composition is cured for the period of time set forth in Table I below.

The resulting cured two-package room temperature vulcanizable silicone composition coating is then tested for adhesion and the results are indicated in Table I below.

TABLE I
Self-Bonding Characteristics of Two-Package Compositions to Various Substrates

Ingredient	Test No. 1	2	3	4	5	6	7
Silane I *	20	—	30	30	30	30	—
Silane II **	—	20	—	—	—	—	—
Ethyl Silicate-40	10	10	10	10	10	10	10
Dibutyl tin dilaurate	10	10	5	2	0.3	0.1	3.3
Xylene	—	—	—	—	—	—	13.3
Mineral Spirits	40	40	—	—	—	—	—
Wt. % of above mixture per 100 parts of Base Polymer Solution	2.0	2.0	1.2	1.2	1.2	1.2	—
Property							
Cure Time, Min.	5	5	7	7	45	120	60
Tack Free Time, Min.	15	10	15	70	200	200	200
Final Cure (Quality)	Excellent	Excellent	Excellent	Excellent	Excellent	Fair	Excellent
Qualitative Adhesion at 24 hours							
Plywood	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Poor
Concrete	Marginal	—	—	—	—	—	Poor
Stainless Steel	Marginal	—	Marginal	Good	Excellent	Excellent	None
Aluminum-coated duralumin	Marginal	Marginal	Excellent	Excellent	Excellent	Excellent	None
Bare Aluminum	Marginal	—	Poor	Excellent	Excellent	Excellent	None
Carbon Steel	Marginal	—	Good	Excellent	Excellent	Excellent	None

TABLE I (Continued)

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$$* \text{ Silane I} - (\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O} - \text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2)\text{CH}_2\text{Cl}$$

** Silane II = $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$

The compositions indicated in Table I, are coated onto a particular substrate, and the resulting product is placed in a humidity chamber partly filled with water so that the coated product is partly immersed in water. This humidity chamber is kept at 120° F at 95+-% relative humidity. After one month in this atmosphere the coated product is again tested for adhesion. These results are also indicated in Table I.

The above results indicate the excellent self-bonding characteristics of the compositions of the present invention, as well as the fact that the bonds that are formed between the silicone rubber composition and the substrate are more hydrolytically stable than the silicone rubber compositions previously devised. It may also be pointed out that the silicone rubber composition of the present invention is self-bonding with superior adhesion to all types of substrates, e.g. masonry, plastic, metal and wood, including plywood, phenolic, concrete, stainless steel, aluminum-coated duralumin, bare aluminum, carbon steel, copper, and tin.

EXAMPLE 2.

A base polymer solution is formed in accordance with the procedure of Example 1, using the concentrations as well as the ingredients indicated in Example 1. There is then formed a curing catalyst mixture in accordance with the ingredients and concentrations shown in Table II below.

The curing catalyst compositions are mixed with the base polymer solutions in the concentrations indicated in Table II below. The resulting room temperature vulcanizable coating compositions are then applied to various substrates and their curing properties are noted as indicated in Table II below.

As shown below in Table II, the room temperature vulcanizable coating compositions are applied to various substrates, such as aluminum-coated duralumin, plywood, bare aluminum and stainless steel. The resulting coated substrates are then placed in a humidity chamber maintained at 120° F, and 95+-% relative humidity. The humidity chamber is partly filled with water so that the panels are partly immersed in water. The resulting coated substrates are kept in the humidity chamber under the conditions specified above for 2 months. After the 2-month period, the panels are tested for quality as illustrated in the results listed in Table II.

TABLE II
Self-Bonding Characteristics of Two-Package Compositions to Various Substrates
and use of Oxygenated Solvents to Extend Pot Life

Ingredient	Test No. 1	2	3	4	5	6	7	8	9**
Silane I *	—	—	—	—	—	—	30	—	—
Silane II **	30	30	30	30	30	30	—	30	—
Ethyl Silicate-40	10	10	10	10	10	10	10	10	10
Dibutyl tin dilaurate	0.5	0.5	0.5	0.5	0.5	—	—	—	3.3
Dibutyl tin diacetate	—	—	—	—	—	0.2	0.2	0.2	—
Methylisocumyl ketone	—	—	—	—	40	—	—	—	—
Ethylene glycol methyl ether	—	—	—	—	—	40	40	—	—
Ethyl acetate	—	—	40	—	—	—	—	—	—
Isopropanol	—	40	—	—	—	—	—	—	—
t-butanol	—	—	—	40	—	—	—	—	—
Xylene	—	—	—	—	—	—	—	—	13.3
Wt. % of above mixture per 100 parts of Base Polymer Solution	2.4	2.4	2.4	2.4	2.4	4.0	4.0	2.4	2.0
<u>Curing Properties</u>									
Pot Life (min.)	40	60 - 90	60 - 70	60	120	90 - 180	25	17	60
Tack Free Time (hrs.)	3 - 4	2 - 18	2 - 18	2 - 3	3 - 4	3 - 4	2 - 3	2 - 3	—
Final Cure	Good	Good	Good	Good	Good	Good	Fair/Good	Good	—

TABLE II (Continued)
Self-Bonding Characteristics of Two-Package Compositions to Various Substrates
and use of Oxygenated Solvents to Extend Pot Life

Ingredient	Test No. 1	2	3	4	5	6	7	8	9***
<u>Qualitative Adhesion at 24 hours</u>									
Aluminum-coated duralumin	Excellent	Excellent	Excellent	Excellent	Excellent	—	—	—	Excellent
Plywood	Excellent	Excellent	Excellent	Excellent	Excellent	—	—	—	—
Aluminum (Bare)	Excellent	—	—	—	—	Excellent	Good	Excellent	Good
Stainless Steel (304)	Excellent	—	—	—	—	Excellent	Good	Excellent	Excellent
<u>Adhesion-Hydrolytic Stability at 2 mos., 120°F, 95% Humidity</u>									
Aluminum-coated duralumin	Excellent	Excellent	Excellent	Excellent	Excellent	—	—	—	Poor
Plywood	Excellent	Excellent	Excellent	Excellent	Excellent	—	—	—	—
Aluminum (Bare)	Excellent	—	—	—	—	Excellent	Poor	Excellent	Very Poor
Stainless Steel (304)	Excellent	—	—	—	—	Excellent	Good	Excellent	Very Poor

* Silane I — $(\text{CH}_3\text{CH}_2\text{O})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NH}_2$

** Silane II — $(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{NH}_2$

*** Metal substrate primed with silicone resin based primer.

5 The results are indicated in Table II, which shows that the present room temperature vulcanizable silicone rubber composition is highly self-bonding to various substrates, as well as hydrolytically stable in the presence of large amounts of moisture and water over prolonged periods of time. The use of oxygen-containing solvents such as ethylene glycol methyl ether, ethyl acetate and butyl ether retards the cure of the composition as illustrated in the results listed in Table II. 5

EXAMPLE 3.

10 There is prepared a base polymer solution in accordance with the procedure set forth in Example 1 using the ingredients and concentrations specified in Example 1. A number of these base polymer solutions are formed, and to each base polymer solution there is added a catalyst mixture defined in Table III below. The resulting mixture is then applied to one of the various substances set forth in Table III, and the adhesion is determined after 24 hours cure. The results are given in Table III below. 10

TABLE III
Self-Bonding Characteristics of Two-Package Compositions to Various Substrates

Ingredient	Test No.									
	1	2	3	4	5	6	7	8	9	10
Silane I	10									
Silane II		30								
Silane III			10							
Silane IV				10						
Silane V					30					
Silane VI						30				
Silane VII							30			
Silane VIII								30		
Silane IX									30	
Silane X										10
Dibutyl-tin dilaurate	-	0.5	0.5	-	0.5	0.5	-	0.5	1.0	-
Ethyl Silicate	40	10	10	10	10	10	10	10	10	10
Wt % of above mixture per 100 parts of Base Polymer Solution	1.0	2.4	2.4	4	0.75	2.4	1.2	2.4	2.4	0.75
Final Cure	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good

y

TABLE III (Continued)

Ingredient	Test No.									
	1	2	3	4	5	6	7	8	9	10
Qualitative Adhesion at 24 hours										
Aluminum-coated duralumin	Exc.	Exc.	-	Exc.	Exc.	-	Good	Exc.	Exc.	Exc.
Plywood	Exc.	Exc.	Exc.	Exc.	Exc.	Good	-	Exc.	Exc.	Exc.
Stainless Steel (304)	Exc.	-	-	-	-	-	-	-	-	-
Exc. — Excellent										
Silane I	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{N} \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2-\text{CH}_2 \end{array}$									
Silane II	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{N} \begin{array}{c} \text{H} \\ \\ \text{CH}_2\text{CH}_2\text{S}-\text{Cl}_3 \end{array}$									
Silane III	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}-\text{C} \begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \text{CH}_2-\text{C} \begin{array}{c} \text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_2\text{N} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \end{array} \end{array}$									
Silane IV	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}-\text{C} \begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2-\text{CH} \begin{array}{c} \text{CH}_3 \\ \\ \text{Cl}_3 \end{array}$									
Silane V	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}-\text{Cl}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{NH}_2$									

TABLE III (Concluded)

Silane VI	-	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}=\text{N}-\text{N}-\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$
Silane VII	-	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{N}-\begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix}$
Silane VIII	-	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{NH}_2$
Silane IX	-	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2\text{NH}_2$
Silane X	-	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}=\text{CH}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

WHAT WE CLAIM IS:-

1. A room temperature vulcanizable silicone rubber composition comprising,
 - (a) a linear, organopolysiloxane containing terminal silicon-bonded hydroxy groups and having a viscosity of 500 to 10,000,000 centipoises when measured at 25° C, the organic groups of the aforesaid organopolysiloxane being substituted or unsubstituted monovalent hydrocarbon radicals,
 - (b) from 5 to 300% by weight, based on organopolysiloxane, of a filler,
 - (c) from 0.1 to 15% by weight, based on organopolysiloxane, of (1) an organoxysilane or silicate corresponding to the general formula,



where R is a monovalent hydrocarbon or halogenated hydrocarbon radical and R¹ is an alkyl, haloalkyl, aryl, haloaryl, alkenyl, cycloalkyl, cycloalkenyl, cyanoalkyl, alkoxy or acyloxy radical, or (2) a liquid partial hydrolysis product of the aforementioned organoxysilane or silicate compounds,

- (d) from 0.1 to 5% by weight, based on the organopolysiloxane, of a catalyst which is metal salt of an organic monocarboxylic or dicarboxylic acid in which the metal ion is lead, tin, zirconium, antimony, iron, cadmium, barium, calcium, titanium, bismuth or manganese, and
- (e) from 0.1 to 10% by weight, based on the organopolysiloxane, of a nitrogen-containing silane of the formula,



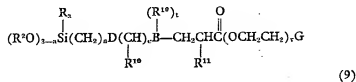
where R is a monovalent hydrocarbon or halogenated hydrocarbon radical, Q is an alkoxy, phenoxy, halo, amino or dialkylamino group, and Q' is a saturated, unsaturated or aromatic hydrocarbon residue substituted by at least one amino, hydrazine, azirane or cyano group and optionally one or more thio, sulphone, oxo, oxo, diorganosilicon and/or ester groups, and a is 0, 1 or 2.

2. The composition of Claim 1 wherein the nitrogen-containing silane has the formula,



where R, R² and R³ are each a monovalent hydrocarbon or halogenated hydrocarbon radical and R⁴, R⁵ and R⁶ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, M is SO₂ or C=O, h is a whole number from 3 to 20, and a is 0, 1 or 2.

14. The composition of Claims 1-10 wherein the nitrogen-containing silane has the formula,



where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, R¹⁰ and R¹¹ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, B is nitrogen, sulfur or oxygen, G is

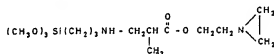


or N(R¹²)₂ where R¹² is hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, c and n are whole numbers from 1 to 10, D is

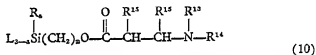


or oxygen, t is 0 when B is sulfur or oxygen and 1 when B is nitrogen, v is a whole number from 1 to 5 and a is 0, 1 or 2.

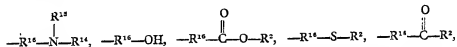
15. The composition of Claim 14 wherein the nitrogen-containing silane has the formula,



16. The composition of Claims 1-10, wherein the nitrogen-containing silane has the formula,

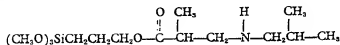


where L is R²N— and R²O—, R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radicals, R¹⁰ is an alkyl or aryl radical of up to 10 carbon atoms, R¹³ and R¹⁴ are each hydrogen, an aryl radical, an alkyl radical, or a radical of the formula

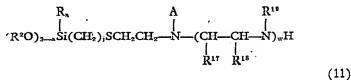


where R¹⁶ is an alkenylene or arylene radicals of up to 10 carbon atoms, n is a whole number from 1 to 20 and a is 0, 1 or 2.

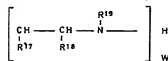
17. The composition of Claim 16 wherein the nitrogen-containing silane has the formula,



18. The composition of Claims 1—10 wherein the nitrogen-containing silane has the formula,

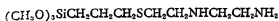


where R and R² are each a monovalent hydrocarbon radical, R¹⁷, R¹⁸ and R¹⁹ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, j is a whole number from 2 to 20, w is a whole number from 1 to 500, A is hydrogen, an alkyl or aryl radical or a radical of the formula

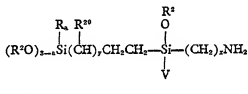


and a is 0, 1 or 2.

19. The composition of Claim 18 wherein the nitrogen-containing silane has the formula,

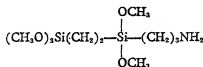


20. The composition of Claims 1—10, wherein the nitrogen-containing silane has the formula,

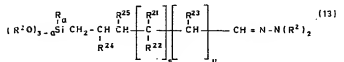


where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, R²⁰ is hydrogen, or an alkyl or aryl radical, V is R or R²O—, y is 0 or a whole number from 1 to 20, x is a whole number from 2 to 20 and a is 0, 1 or 2.

21. The composition of Claim 20 wherein the nitrogen-containing silane has the formula,

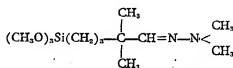


22. The composition of Claims 1—10, wherein the nitrogen-containing silane is of the formula.

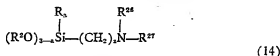


where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, R²¹, R²², R²³, R²⁴ and R²⁵ are each hydrogen, or an alkyl, cycloalkyl or aryl radical of up to 10 carbon atoms, s is 0 or 1, u is 0 or a whole number from 1 to 20 and a is 0, 1 or 2.

23. The composition of Claim 22 wherein the nitrogen-containing silane has the formula.



24. The composition of Claims 1—10, wherein the nitrogen-containing silane has the formula,

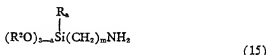


5 where R and R²⁶ are each a monovalent hydrocarbon or halogenated hydrocarbon radical, R²⁶ and R²⁷ are each hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, *a* is a whole number from 2 to 20 and *a* is 0, 1 or 2. 5

25. The composition of Claim 24 wherein the nitrogen-containing silane has the formula,



26. The composition of Claims 24, wherein the nitrogen-containing silane has the formula,

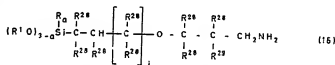


15 where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, *m* is a whole number from 2 to 20 and *a* is 0, 1 or 2. 15

27. The composition of Claim 26 wherein the nitrogen-containing silane has the formula,

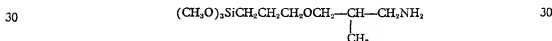


28. The composition of Claims 1—10, wherein the nitrogen-containing silane has the formula, 20

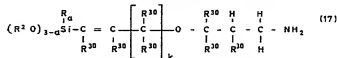


25 where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, R²⁶ is an alkyl or cycloalkyl radical or where two R²⁶ radicals are attached to the same carbon atom, taken together with the carbon atom to which they are attached, they may form a cycloalkyl radical having 5 to 7 carbon atoms, R²⁷ is an alkyl radical having 1 to 8 carbon atoms, *i* is a whole number from 1 to 4 and *a* is 0, 1 or 2. 25

29. The composition of Claim 28 wherein the nitrogen-containing silane has the formula,



30. The composition of Claims 1—10, wherein the nitrogen-containing silane has the formula,

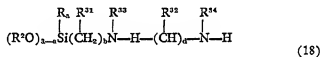


where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, each symbol R^{3b} is hydrogen, a C₁-C₈ alkyl radical, a cycloalkyl radical containing up to 7 carbon atoms, a mononuclear or binuclear aryl radical, a mononuclear aryl C₁-C₈ alkyl radical or two radicals R^{3b} attached to the same carbon atom can, taken together with that carbon atom, form a cycloalkyl radical, b is a whole number from 1 to 9 and a is 0, 1 or 2.

31. The composition of Claim 30 wherein the nitrogen-containing silane has the formula,

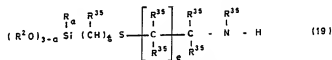


32. The composition of Claims 1-10, where the nitrogen-containing silane has the formula,



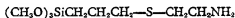
where R and R² are each a monovalent hydrocarbon radical, R^{3c}, R^{3d}, R^{3e} and R^{3f} are each hydrogen or an alkyl or aryl radical of up to 10 carbon atoms, b is a whole number from 2 to 10, d is a whole number from 2 to 10 and a is 0, 1 or 2.

33. The composition of Claims 1-10 wherein the nitrogen-containing silane has the formula,

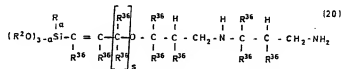


where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, each symbol R^{3k} is hydrogen, or an alkyl or aryl radical of up to 10 carbon atoms, e is a whole number from 1 to 10, f is a whole number from 2 to 10 and a is 0, 1 or 2.

34. The composition of Claim 33 wherein the nitrogen-containing silane has the formula,

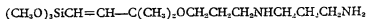


35. The composition of Claims 1-10, wherein the nitrogen-containing silane has the formula,



where R and R² are each a monovalent hydrocarbon or halogenated hydrocarbon radical, each symbol R^{3r} is hydrogen, or an alkyl radical, aryl radical, cycloalkyl radical containing 5 to 7 carbon atoms, mononuclear or binuclear aryl radical, or mononuclear aryl C₁-C₈ alkyl radical or two radicals R^{3r} attached to the same carbon atom can, taken together with that carbon atom, form a cycloalkyl radical, s is 1, 2, 3 or 4 and a is 0, 1 or 2.

36. The composition of Claim 35 wherein the nitrogen-containing silane has the formula,



37. The silicone rubber composition of Claims 1—36 wherein there is further present 0.5% to 5% by weight of the total composition of an alkanol, ether, ketone, ester or alcohol ester as solvent.

38. A process for producing a composition as claimed in any of claims 1 to 37 which comprises mixing the linear organopolysiloxane (a), the filler (b), component (c), the catalyst (d), and the nitrogen-containing silane (e).

39. A method for coating a roof which comprises applying a composition according to claim 37 over a roof, and allowing said composition to cure.

40. A method as claimed in claim 39 wherein roofing granules are applied over said composition after it is applied over the roof and before it cures.

41. A method as claimed in claim 39 substantially as herein described.

42. A process as claimed in Claim 38, substantially as herein described.

43. A composition as claimed in Claim 1 substantially as herein described.

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